4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

MEASUREMENTS OF ACTIVITIES OF CHROMIUM OXIDES IN $CaO-SiO_2-CrO_x$ SLAGS AT STEELMAKING TEMPERATURES

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Synopsis: As a fundamental study on thermodynamic properties of CrO_x-bearing slags, the activities of chromium oxides in liquid $CaO-SiO_2-CrO_x$ slag system were measured with electromotive force method by equilibrating with metallic chromium crucible at 1600°C. The effects of slag basicity and temperature were investigated. Experimental results showed that the slag basicity has a significant effect on the activities of the chromium oxides. The higher the slag basicity, the higher the activities of the chromium oxides. The effect of temperature is not very prominent in the temperature range of 1500-1600°C. The activities slightly decrease with increasing temperature. In addition, the oxidation state of chromium in the slags was examined and discussed. Higher temperature and lower slag basicity favour divalent chromium oxide instead of trivalent chromium oxide.

Key words: activity, oxidation state, chromium oxides, slag, solid electrolyte

1. Introduction

Knowledge of the activities of chromium oxides in slag melts is of great value for both theoretical evaluation and practical applications in stainless steelmaking. Owing to the continuously increasing demand for stainless steel production in recent years, there has been a persistent search for effective and economic ways to raise the chromium recovery. This depends very much on the slag/metal reactions. Because of the multi-valence state of chromium ions in slags, the behaviour of chromium in metallurgical slags is complicated. So far, little systematic attempts have been made due to the experimental difficulties such as high melting point of chromium oxide containing slags as well as crucible corrosion. Data of activities of chromium oxides in slags are extremely scarce. Only few articles[1-3] were found on activities of chromium oxides, the measurements being made only sporadically and at low temperatures. Concerning oxidation state of chromium in slags, there are a few papers available[4-7] but the data are still inadequate.

In the present study, the activities of chromium oxides were determined by galvanic cell with ZrO_2(9mol%MgO) electrolyte covering the isothermal liquidus section in the $CaO-SiO_2-CrO_x$ quasi-ternary system and temperature range from 1500°C to 1600°C. Furthermore, the oxidation state of chromium in the slags was investigated.

2. Principles

The galvanic cell was constructed as follows:

$$Ir, (Cr+Cr_2O_3)||ZrO_2(9MgO)||(CrO_x)slag+(Ag/Cr)alloy, (ZrO_2+Mo)cermet(Mo)$$

Considering the influence of electronic conduction in the electrolyte at high temperature, the open-circuit electromotive force of the cell is given by the following equation according to the Nernst equation:

$$E=\frac{RT}{F}\ln\frac{Po_2(ref)^{1/4}+Pe^{1/4}}{Po_2(slag)^{1/4}+Pe^{1/4}} \qquad (1)$$

where,
E, the electromotive force measured;
R, gas constant, 8.314 J/K/mol;
F, Faraday constant, 96500 J/V/mol;
T, temperature, K;
Po_2(slag), the oxygen partial pressure referring to the slag system to be measured;
Po_2(ref), the oxygen partial pressure referring to the Cr/Cr_2O_3 equilibrium at the reference electrode:
$\lg(Po_2/atm)=8.613-3.866\mathrm{x}10^4/(T/K)$[8]
Pe, the characteristic oxygen partial pressure at which the ionic and n-type electronic conductivities are equal[9]:
$\lg(Pe/atm)=20.40-6.45\mathrm{x}10^4/(T/K)$[10]

The equilibrium relations underlying the experiments can be represented as follows:

$$Cr + 1/2O_2 = (CrO) \qquad (2)$$

$$\Delta G_1{}^o=-RT\ln K_1=-79880+15.25T\ (cal)^{[11]} \qquad (3)$$

$$K_1=\frac{a_{(CrO)}}{a_{Cr}\cdot Po_2^{1/2}} \qquad (4)$$

$$2Cr + 3/2O_2 = (Cr_2O_3) \qquad (5)$$

$$\Delta G_2{}^o=-RT\ln K_2=-265330+59.11T\ (cal)^{[8]} \qquad (6)$$

$$K_2=\frac{a_{(Cr_2O_3)}}{a_{Cr}{}^2\cdot Po_2^{3/2}} \qquad (7)$$

where, the activities of Cr_2O_3 and Cr refer to pure solid state, and that of CrO refers to pure liquid state. $\Delta G_1{}^o$ was obtained in the temperature range of 1665-1750°C[11]. As an approximation, it was adopted in the present study, since this is the only data available. The presence of silver was beneficial for completing the electrical circuit and making the equilibrium faster. In the present experiment, activity of chromium was unity, since the alloy was saturated with Cr crucible. According to equation (1), if the electromotive force was measured, the oxygen partial pressure in the slag system could be calculated. Then by combining equations (3) and (4), (6) and (7), the activities of chromium oxides in the slags could be determined.

3. Experimental

The slag and alloy samples to be equilibrated were prepared from various reagent grade oxides and metal powders. These starting materials had been previously prepared in appropriate amounts. Suitable precautions were taken to make the samples homogeneous in all steps of the preparation. The samples with known composition were pressed into pellets and packed in a Cr crucible. 30g slag and 16g Ag-Cr alloy were used.

A vertical tube furnace with conventional design was used for equilibration. The chromium working crucible was located in a corundum protecting crucible lined with Mo sheet. The temperature of the melt was measured by a calibrated PtRh30-PtRh6 thermocouple. The overall errors of the temperature measurements were evaluated to be about ±4°C. Ar gas was used to maintain inert atmosphere to protect the reaction system. A purification train for argon consisted of KOH, silica gel, phosphorus pentoxide, and sponge titanium kept at 850°C in a resistance furnace. For the oxygen partial pressure measurement in the molten slag/metal system, $ZrO_2(MgO)$ electrolyte probes were adopted. A mixture of Cr and Cr_2O_3 in 4:1 weight ratio connected with Ir wire was used as reference electrode in the electrolyte probe.

A ZrO_2/Mo cermet rod welded to a Mo wire was used as the measuring electrode and was immersed into the slag and Ag-Cr alloy melt. Fig.1 shows the schematic experimental apparatus.

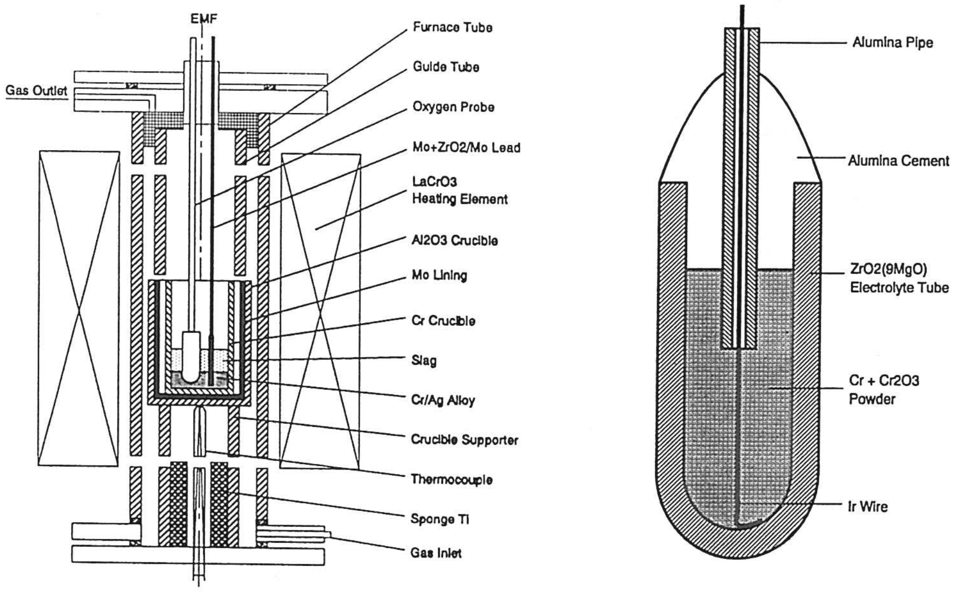


Fig.1 Schematic representation of the experimental arrangement and the construction of the oxygen probe

A microvolt meter with $1G\Omega$ input impedance was used for emf measurements. To correct the emf from the different electrical leads, the thermal emf of the Mo/ZrO_2(Mo)-Ir couple was measured through a separate experiment. The result of the thermo-electromotive force with temperature was formulated into the following equation in the temperature range of 1500°-1600°C: $E(Mo/ZrO_2(Mo)\text{-}Ir)(mv) = -6.65 + 1.83 \times 10^{-2}T$.

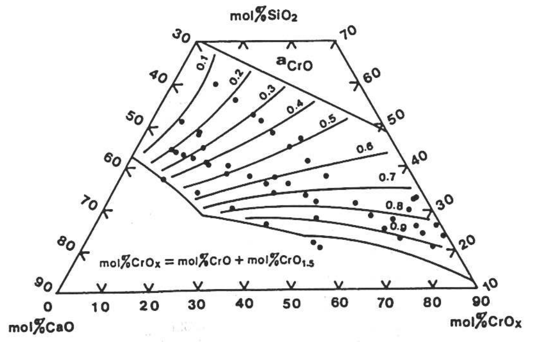
When the system reached equilibrium, the stable emf was obtainable within a few seconds after immersion. After that, slag samples were taken with an alumina tube with controlled suction, and quickly quenched in cold water. The chemical compositions of the slag samples including the percentages of divalent chromium, total chromium, CaO and SiO_2, were determined by wet chemical analysis.

4. Results and discussion

The activity of CrO was determined with respect to the pure liquid standard state, but that of Cr_2O_3 referred to the pure solid state. For conformity, it was converted to $a_{CrO_{1.5}}$: $2\ln a_{CrO_{1.5}} = \ln a_{Cr_2O_3}$. Respectively, it follows: mol%CrO_x = mol%CrO + mol%$CrO_{1.5}$.

4.1 Iso-activity diagrams of CrO and $CrO_{1.5}$ in CaO-SiO_2-CrO_x slag system

Fig.2 shows the iso-activity curves of CrO and $CrO_{1.5}$ in CaO-SiO_2-CrO_x slags in equilibrium with chromium saturated alloy at 1600°C. The thermodynamic consistency between phase diagram and activity is maintained within the homogeneous liquid region. The activities of chromium oxides depend, naturally, on the total chromium oxide content but also on the ratio of N_{CaO}/N_{SiO_2} in the slag system. Here, N represents the mole fractions of the oxides in the slag. The concentration of chromium oxides in the slag determines the oxygen partial pressure in the system under the present experimental conditions. The substitution of SiO_2 for CaO results in lower activities of chromium oxides. At high CaO contents, the slags are readily saturated with CrO_x due to its low solubility[12]. The activities of chromium oxides , therefore, are higher in the range of high slag basicity. When basicity increases, the solubility of the chromium oxides increases rapidly, which contributed to the decrease in the activity of CrO, and in the activity of $CrO_{1.5}$.



(a) CrO activities (b) $CrO_{1.5}$ activities

Fig.2 Iso-activity diagrams of CrO and $CrO_{1.5}$ in $CaO\text{-}SiO_2\text{-}CrO_x$ quasi-ternary system at 1873K

4.2 Effect of temperature

Compared with the basicity effect, the effect of temperature on the activities of chromium oxides was not so prominent in the temperature range of 1500-1600°C, shown in Fig.3. When the temperature increased, the activities of chromium oxides decreased slightly. The temperature effect on the activities of the chromium oxides can be contributed to the increased solubility of the chromium oxides in the slags as raising temperature.

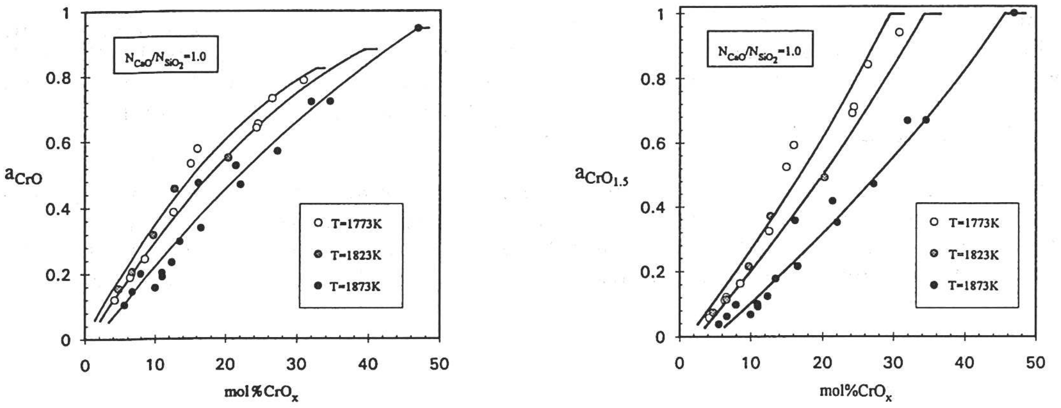


Fig.3 The effect of temperature on the activities of CrO and $CrO_{1.5}$ in $CaO\text{-}SiO_2\text{-}CrO_x$ quasi-ternary system at $N_{CaO}/N_{SiO_2}=1$

4.3 Effect of slag basicity

Fig.4 shows the effect of slag basicity on the activities of chromium oxides. It is obvious that the slag basicity has remarkable effect on the activities of chromium oxides. The higher the slag basicity, the higher the chromium oxides activities. This can be qualitatively explained by the ionic structure of slags. Though the behaviour of different chromium oxides in slags is quite weakly known, it can be anticipated that at lower slag basicities, almost all the metal cations are associated with the large SiO_2 anionic groups, so that only a few free O^{2-} ions exist. This results in low activities of chromium oxides in these slag melts due to strong complexation with SiO_2. As basic oxides increase, the SiO_2 networks are broken into smaller anion groups and the proportion of free oxygen starts to increase. Therefore, the activities of chromium oxides will increase because the stronger basic metal oxides will liberate chromium oxides from SiO_2 network in the slag. When the slag basicity N_{CaO}/N_{SiO_2} is 0.2 or less, the activities of chromium oxides can not be obtained properly at low CrO_x content due to silica saturation. On the other hand, the activities of chromium oxides are related to the solubility of chromium oxides in the slag. It is obvious that the higher the slag basicity, the lower the solubility of chromium oxides.

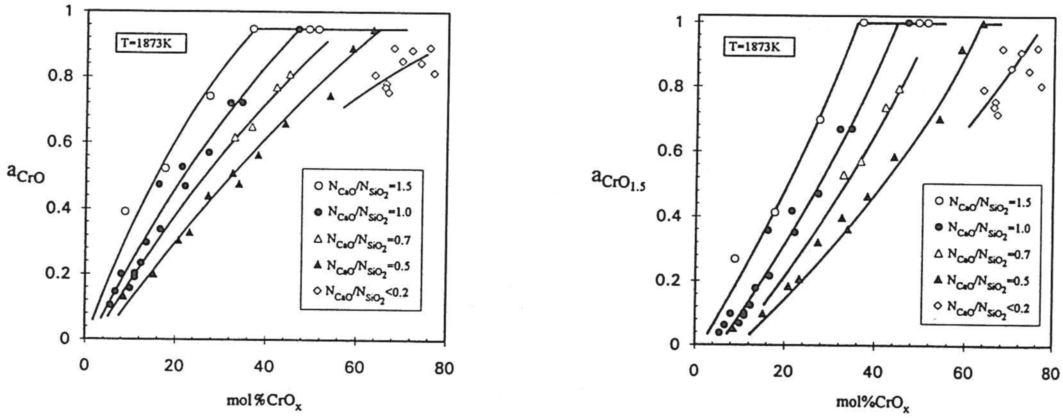


Fig.4 The effect of slag basicity on the activities of CrO and $CrO_{1.5}$ in CaO-SiO_2-CrO_x quasi-ternary system at 1873K

4.4 Oxidation state of chromium in CaO-SiO_2-CrO_x slags

The following equilibrium of chromium oxides can be expected in slag/metal equilibrium system: $(Cr_2O_3) + Cr = 3(CrO)$. The divalent chromium fraction depends on the oxygen partial pressure, temperature and basicity of the slag. Figs.5 and 6 show the divalent chromium fraction in the slag system versus the total chromium oxides content at different temperatures and slag basicities, respectively. The divalent chromium fraction increased slightly with increasing temperature at a given slag basicity, but decreased with growing slag basicity and total chromium oxides content.

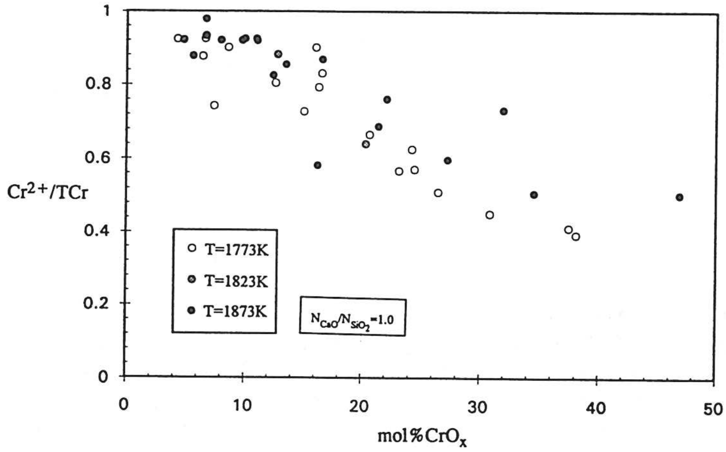


Fig.5 The effect of temperature on oxidation state of chromium in slags

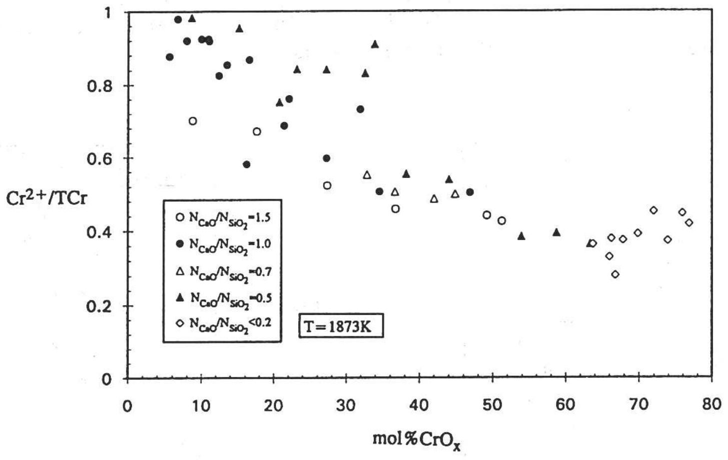


Fig.6 The effect of slag basicity on oxidation state of chromium in slags

5. Conclusions

The following conclusions can be drawn from the experimental results:

(1) The iso-activity diagrams for CrO and $CrO_{1.5}$ in the liquid area of CaO-SiO_2-CrO_x slag system were determined at 1873K. Except for the chromium oxide content in the slag, the activities of chromium oxides depend on the basicity of the slag. The substitution of SiO_2 for CaO results in increase in the solubility of the chromium oxides and decrease in the activities of chromium oxides.

(2) The effect of temperature on the activities of chromium oxides and the oxidation state of chromium in slags was not very substantial at $N_{CaO}/N_{SiO_2}=1$. Increasing temperature resulted in lower activities of chromium oxides and higher divalent chromium fraction in the slag.

(3) Slag basicity had significant effect on both chromium oxides activities as well as on the oxidation state of chromium in slags at 1600°C. The higher the slag basicity, the higher the chromium oxides activities, but the lower the divalent chromium fraction in the slag.

6. References

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